TWO IRON NITRIDES.

By Shun-ichi SATOH.

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I. Introduction. Compounds of iron and nitrogen, so far as is known in literature, are $Fe_{12}N$[1], Fe_8N[2], Fe_6N[2], Fe_4N[3], Fe_7N_2[4], Fe_6N_2[4], Fe_5N_2[5], Fe_2N[6], Fe_3N_2[7] and FeN[8]. Of these, Fe_4N and Fe_2N are definitely known compounds. Fe_2N is obtained by passing gaseous ammonia over iron powder at 450°C. It is a paramagnetic substance[10] forming a hexagonal close packed lattice[9]. Its heat of formation is 3040 cal.[11] Fe_4N is obtained by heating Fe_2N in vacuo at 440°–550°C. It forms a face centred cubic lattice[12], being a ferromagnetic substance[10]. Its heat of formation is not yet determined. The equilibrium diagram of iron and nitrogen system was studied by C. B. Sawyer[13] (thermal analyses), T. Murakami and S. Iwaizumi[14] (magnetic analyses), A. Fry[10] (microscope and magnetic analyses) and by E. Lehrer[15] (magnetic analyses and X-ray). Fig. 1 shows a most reliable equilibrium diagram obtained by E. Lehrer[15].

The equilibrium between iron, iron nitride, ammonia and hydrogen at a high temperature was studied by E. Baur and G.L. Voerman[16], A.A. Noyes

(1) N. Tschischewski, *J. Iron and Steel Inst.*, **92** (1915), 77.
(2) A. A. Noyes and L. B. Smith, *J. Am. Chem. Soc.*, **43** (1921), 480.
(3) C. Charpy et L. Bonnerot, *Compt. rend.*, **158** (1914), 996; A. Fry, *Stahl und Eisen*, **43** (1923), 1272.
(4) A. W. F. Rogstadius, Dissertation Upsala, (1860).
(5) H. Braune, *Stahl und Eisen*, **26** (1906), 1360.
(6) G. J. Fowler, *J. Chem. Soc.*, **79** (1901), 288.
(7) A. H. White and L. Kirschbraun, *J. Am. Chem. Soc.*, **28** (1906), 1347.
(8) A. Guntz, *Compt. rend.*, **135** (1902), 739.
(9) G. Hägg, *Nova acta regiae societates scientiarum Upsaliensis*, IV, **7**, No. 1; A. Osawa and S. Iwaizumi, *Z. Kryst.*, **69** (1928), 26.
(10) A. Fry, loc. cit.
(11) G. Fowler, Ph. J. Hartog, *J. Chem. Soc.*, **79** (1901), 299.
(12) R. Brill, *Naturw.*, **16** (1928), 593; A. Osawa and S. Iwaizumi, loc. cit.; O. Eisenhut und E. Kaupp, *Z. Elektrochem.*, **36** (1930), 392. G. Hägg, loc. cit.
(13) C. B. Sawyer, *Tran. Am. Inst. Min. Met. Eng.*, **69** (1923), 810.
(14) T. Murakami and S. Iwaizumi, *Kinzoku no Kenkyu*, **5** (1928), 159.
(15) E. Lehrer, *Z. Elektrochem.*, **36** (1930), 460.
(16) E. Baur und G. L. Voerman, *Z. physik. Chem.*, **52** (1905), 471.

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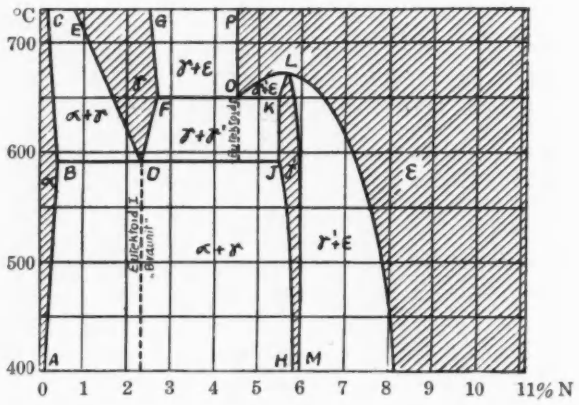

Fig. 1.

Equilibrium diagram of iron and nitrogen according to E. Lehrer.

and L.B. Smith[1], E. Lehrer[2], P. H. Emmett, S.B. Hendricks, S. Brunauer[3] and S. Brunauer, M. E. Jefferson, P. H. Emmett, S. B. Hendricks[4]. The authors of the first two papers did not clearly determine the composition of the solid phase that takes part in equilibrium, but E. Lehrer[2] determined that Fe_2N and Fe_4N as well as Fe_4N and Fe could coexist but Fe and Fe_2N could not coexist to take part in equilibrium.

The author measured the heat of formation of Fe_4N by means of calorimeter. Then he obtained the equilibrium equations of the systems iron, iron nitrides, ammonia and hydrogen from the observed heat of formation of Fe_4N and compared them with the experimental data obtained at high temperatures. Next, he studied the electrochemical properties of iron nitrides.

II. Specimens. The author prepared iron nitride with the apparatus shown in one of his previous papers[5] as Fig. 1. Iron oxide, which he obtained by igniting iron oxalate, was reduced with electrolytic hydrogen. Pure iron thus obtained was treated with gaseous ammonia at 450°C. for 40 hrs. Gaseous ammonia was obtained by evaporating liquid ammonia; it was purified through solid potassium hydroxide, calcium oxide, barium

(1) A. A. Noyes and L. B. Smith, loc. cit.
(2) E. Lehrer, *Z. Elektrochem.*, **36** (1930), 388.
(3) P. H. Emmett and others, *J. Am. Chem. Soc.*, **52** (1930), 1456.
(4) S. Brunauer and others, *J. Am. Chem. Soc.*, **53** (1931), 1778.
(5) S. Satoh, this Bulletin, **5** (1930), 291.

oxide and molten metallic sodium. Iron nitride which was produced in this way, contains 10.65% nitrogen ; it is paramagnetic substance and called ε . Then he decomposed ε in vacuo at 500°C., at which Fe_4N does not decompose, and obtained nitrides which contain respectively 6.15% and 6.53% nitrogen and which are called $\varepsilon+\gamma'$. Next, he decomposed $\varepsilon+\gamma'$ in vacuo at 550°C., at which Fe_2N decomposes, and obtained nitride, containing 5.52% nitrogen, which is called $\gamma'+\alpha$. The decomposition was carried out by means of the apparatus referred to as Fig. 2 in the previous paper[1]. Iron nitride which contains 6.53% nitrogen was used in the calorimetric investigation ; the other nitrides were used to study their electrochemical properties.

The author analysed the nitrides, employing the method adopted by F. Wüst and J. Duhr[2]. A fused silica tube specially made was used for distillation to prevent yielding alkalies in the distillate. By analysing oft-sublimated ammonium chloride, reliable results were obtaind. The apparatus is shown in Fig. 2.

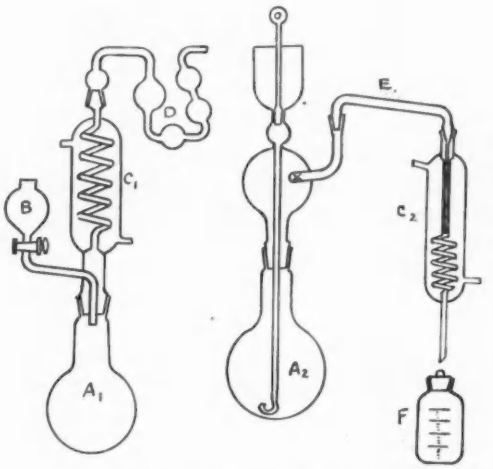

Fig. 2. Apparatus used for analysis of nitrogen in iron.

The powder photograms were taken with two cameras, diameters of which were respectively 60.1 and 60.4 mm. Fe-K-radiation was used from a tube of Siegbahn type, which was run with about 30,000 volts and 4 milli-

(1) S. Satoh, this Bulletin, **5** (1930), 291.
(2) F. Wüst und J. Duhr, *Mitt. Kaiser Wilhelm Inst. Eisen fors.*, **2** (1921), 39.

amperes. Powder photograms are indicated in Fig. 3. The $\sin^2\theta$ values which the author has obtained from the photograms, using Hadding's correction:

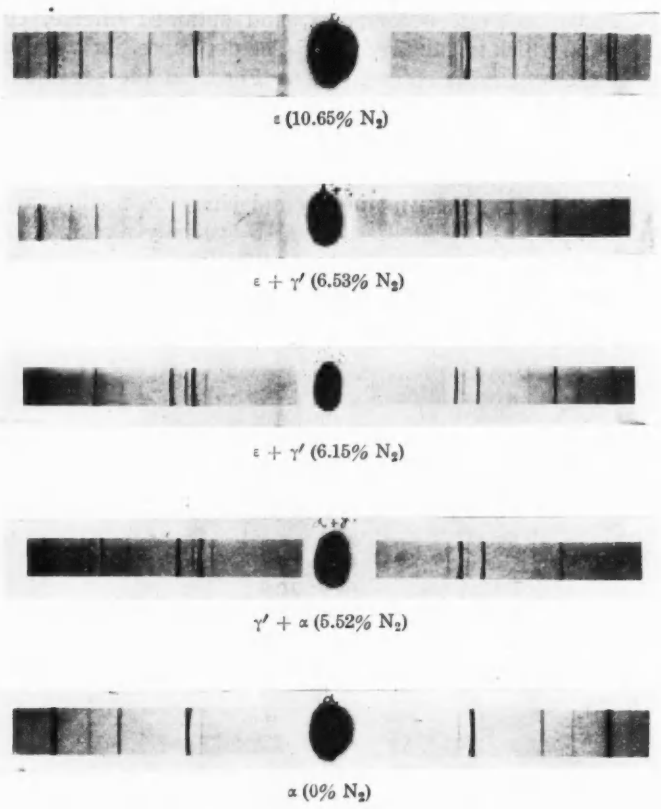

Fig. 3. Powder photograms of iron nitrides.
Fe-K-radiation.

$$2\gamma_{\text{corr.}} = 2\gamma_0 - \rho(1 \pm \cos 2\theta)$$

are given in Tables 1–5, together with the calculated values. The calculated values of $\sin^2\theta$ in Table 1 were obtained by the formula:

Table 1. Powder photograms of iron nitride (ε) (10.65% N_2). Fe-K-radiation.

Film dia. 60.4 mm.

Intensity	Radiation	$h\,k\,l$.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
St.	α	100	0.1622	0.1626	Hex.
M.	β	101	0.1728	0.1731	,,
St.	α	002	0.1908	0.1914	,,
St.	α	101	0.2101	0.2105	,,
W.	β	102	0.2905	0.2911	,,
St.	α	102	0.3527	0.3540	,,
W.	β	110	0.4009	0.4011	,,
St.	α	110	0.4866	0.4878	,,
St.	α	103	0.5917	0.5932	,,
W.	α	200	0,6487	0.6504	,,
St.	α	112	0.6767	0.6791	,,
St.	α	201	0.6967	0.6982	,,
W.	α	004	0.7623	0.7655	,,

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4}{3}\cdot\frac{h^2+hk+k^2}{a^2}+\frac{l^2}{c^2}\right]$$

where λ is the wave-length of the iron radiation — $K_\alpha = 1.932$ Å. and $K_\beta = 1.753$ Å; a and c are elementary dimensions — $a = 2.767$ Å. and $c = 4.417$ Å. The calculated values of $\sin^2\theta$ of ε-phase in Tables 2 and 3 were obtained by the above formula where $a = 2.713$ Å. and $c = 4.376$ Å. The calculated values of $\sin^2\theta$ of γ'-phase in Tables 3 and 4 were obtained by the formula:

Table 2. Powder photograms of iron nitride ($\gamma' + \varepsilon$) (6.53% N_2). Fe-K-radiation.

Film dia. 60.4 mm.

Intensity	Radiatian.	$h\,k\,l$.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
W.	β	111	0.1599	0.1606	F. C. C.
v. w.	α	100	0.1689	0.1691	Hex.
v. w.	β	101	0.1817	0.1792	,,
St.	α	111	0.1940	0.1952	F. C. C.
St.	β	200	0.2185	0.2141	,,
St.	α	200	0.2607	0.2603	,,
M.	α	102	0.3644	0.3641	Hex.
W.	β	220	0.4273	0.4282	F. C. C.
W.	α	110	0.5084	0.5073	Hex.
St.	α	220	0.5212	0.5206	F. C. C.
W.	β	311	0.5868	0.5888	,,
M.	α	103	0.6094	0.6079	Hex.
W.	α	112	0.7029	0.7023	,,
St.	α	311	0.7134	0.7146	F. C. C.
W.	α	201	0.7252	0.7252	Hex.
St.	α	222	0.7796	0.7795	F. C. C.

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2) .$$

where the side of elementary cube a is 3.789 Å. The calculated values of $\sin^2\theta$ of pure iron in Table 5 were obtained by the above formula where $a = 2.86$ Å. The accordance between the observed and calculated values of

Table 3.

Powder photograms of iron nitride ($\gamma'+\varepsilon$) (6.15% N_2)
Fe-K-radiation.

Film dia. 60.1 mm.

Intensity	Radiation	$h\ k\ l$.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
W.	β	111	0.1626	0.1606	F. C. C.
St.	α	111	0.1965	0.1952	,,
M.	β	200	0.2175	0.2141	,,
St.	α	200	0.2624	0.2603	,,
W.	α	102	0.3630	0.3641	Hex.
W.	β	220	0.4298	0.4282	F. C. C.
W.	α	110	0.5029	0.5073	Hex.
St.	α	220	0.5224	0.5206	F. C. C.
W.	β	311	0.5885	0.5888	,,
W.	α	103	0.6039	0.6079	Hex.
v. w.	β	222	0.6428	0.6424	F. C. C.
W.	α	112	0.6951	0.7023	Hex.
St.	α	311	0.7150	0.7146	F. C. C.

$\sin^2\theta$ is very good. From the above experiment it may be clearly seen that ε-phase only forms a hexagonal close packed lattice and it contains neither a face centred cubic lattice of Fe_4N nor a body centred cubic lattice of iron, that $\varepsilon+\gamma'$-phase is a mixture of a hexagonal close packed lattice of Fe_2N and a face centred cubic lattice of Fe_4N and does not contain a body centred cubic lattice of iron, and that similarly $\gamma'+\alpha$-phase does not contain a hexagonal close packed lattice of ε-phase.

Table 4.

Powder photograms of iron nitride ($\alpha+\gamma'$) (5.52% N_2)
Fe-K-radiation.

Film dia. 60.1 mm.

Intensity.	Radiation	*h k l.*	$\sin^2\vartheta$ obs.	$\sin^2\vartheta$ calc.	Lattice
M.	β	111	0.1605	0.1606	F. C. C.
St.	α	111	0.1940	0.1952	,,
W.	β	200	0.2151	0.2141	,,
St.	α	200	0.2599	0.2603	,,
W.	β	220	0.4281	0.4282	,,
St.	α	220	0.5224	0.5206	,,
W.	β	311	0.5894	0.5888	,,
v. w.	β	222	0.6428	0.6424	,,
St.	α	311	0.7142	0.7146	,,

Table 5.

Powder photograms of iron. (α)
Fe-K-radiation.

Film dia. 60.40 mm.

Intensity	Radiation	*h k l.*	$\sin^2\vartheta$ obs.	$\sin^2\vartheta$ calc.	Lattice
W.	β	110	0.1876	0.1878	B. C. C.
St.	α	110	0.2272	0.2282	,,
W.	β	200	0.3743	0.3756	,,
M.	α	200	0.4547	0.4564	,,
W.	β	211	0.5598	0.5633	,,
St.	α	211	0.6800	0.6846	,,
v. w.	β	110	0.7465	0.7511	,,

III. Determination of the Heat of Formation of Fe_4N. When iron nitride is dissolved in dilute sulphuric acid, it is decomposed and yields salts of iron and of ammonium, hydrogen being evolved at the same time. This reaction offers a convenient method for the determination of the heat of formation of the nitride. The equation corresponding to the reaction is as follows:

$$2[Fe_4N] + (10H_2SO_4Aq) = (8FeSO_4Aq) + (2NH_4HSO_4Aq) + 5H_2$$

The concentration of acid was 1.022 normal. Six hundred grams were introduced into a glass calorimeter, a very thin glass beaker of about 19 gr. in weight, provided with a cover and supported on three corks inside a Dewar's vessel. The liquid was agitated by a glass screw-stirrer revolving about four times a second, and a regular current of hydrogen was led through the calorimeter to prevent the oxidation of the ferrous sulphate formed. The calibrated Beckmann's thermometer was used. The apparatus is shown in Fig. 4.

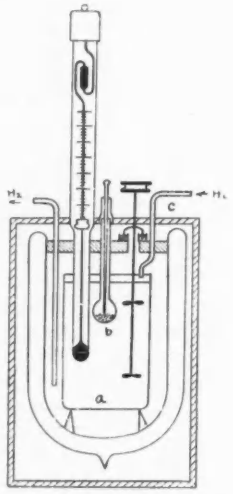

Fig. 4. Apparatus for measurement of heat of solution of iron nitride.

The thermometer was carefully observed until the rate of change was steady. Then the iron nitride, contained in *b*, was introduced into the calorimeter by breaking *b* by a glass rod and readings were taken every minute until the rate of change was steady. The reaction was a slow one; the time needed to accomplish each experiment was about 4 hrs. The correction was calculated graphically and the agreement of four results shows that the determinations are satisfactory. The solution yielded almost no coloration with potassium thiocyanate at the conclusion of the experiments.

The specific heat of the final solution was taken to be equal to that of the solution of sulphuric acid used. The specific heat was taken from the experiments of G. Agde and H. Holtmann[1], which gives 0.9598. The specimen used contains 6.53% nitrogen: mixture of 12.04% Fe_2N and 87.96% Fe_4N. The heat of solution of Fe_2N in dilute sulphric acid was taken from the determination of G. Fowler, Ph. J. Hartog[2] as 81.56 Cal. for 125.7 gr. of Fe_2N.

The details of the experiments are shown in Table 6.

Table 6. Details of the calorimetric experiments.

Number of experiment.	60	61	62	63	Mean
Composition of the nitride % N_2	6.53	6.53	6.53	6.53	
Water equivalent of calorimeter and contents. (including acid, stirrer, part of thermometer immersed etc.)	580.0	580.3	580.3	580.4	

(1) G. Agde und H. Holtmann, *Z. anorg. allgem. Chem.*, **158** (1926), 316.
(2) G. Fowler, Ph. J. Hartog, loc. cit.

Table 6.—(*Continued.*)

Number of experiment.	60	61	62	63	Mean
Weight of substance dissolved (gr.)	1.0005	1.0046	1,0032	1.0023	
Rise of temperature. (°C.)	0.930	0.954	0.927	0.937	
Cooling correction. (°C.)	0.031	0.034	0.028	0.023	
Total number of calories evolved. (Cal.)	0.5574	0.5734	0.5542	0.5572	
Calories evolved by the solution of Fe_2N. (Cal.)	0.0782	0.0785	0.0784	0.0783	
Calories evolved by the solution of 1gr. Fe_4N. (Cal.)	0.5446	0.5600	0.5392	0.5432	0.5468
Thermal value of the reaction in calories.	129.74				

If we start from a given initial system and pass to a given final system by two different cycles of transformations, we may assume that the total heat evolved is in both cases the same.

We take as the initial system $4[Fe]+N+10H+5[S]+20+Aq$.
We take as the final system $(4\,FeSO_4Aq)+(NH_4HSO_4Aq)+5H$.

Cycle I — Thermal value of reaction.

$$4[Fe]+N=[Fe_4N] \qquad x$$

$$5\{H_2+[S]+2O_2\}+Aq=(5H_2SO_4Aq) \qquad 5a_1$$

$$[Fe_4N]+(5SO_4H_2)+Aq=(4SO_4FeAq)+(NH_4HSO_4Aq)+5H \qquad 129.74$$

Cycle II

$$4[Fe]+4[S]+16O+Aq=(4SO_4FeAq) \qquad 4a_2$$

$$N+10H+[S]+4O+Aq=(NH_4HSO_4Aq)+5H \qquad a_3$$

$$(FeSO_4Aq)+(NH_4HSO_4Aq)=(FeSO_4Aq)+(NH_4HSO_4Aq) \qquad 0$$

We have the equation $x+5a_1+129.74=4a_2+a_3$
According to Berthelot, $a_1=210.1$ Cal, $a_2=234.9$ Cal, $a_3=245.1$ Cal, we find $x=4.46$ Cal, i.e.,

$$4[Fe]+N=[Fe_4N]+4460\text{ cal.}$$

IV. Discussion of the Results. By combining the measured heat of formation of Fe_4N:

$$4[Fe] + N = [Fe_4N] + 4460 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

with the heat of formation of ammonia:

$$2NH_3 = N_2 + 3H_2 - 22000 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

the author obtained the following result:

$$8[Fe] + 2NH_3 = 2[Fe_4N] + 3H_2 - 13080 \quad \ldots\ldots\ldots \quad (4)$$

Similarly by combining the heat of formation of Fe_2N measured by G. Fowler, Ph. J. Hartog[1]

$$2[Fe] + N = [Fe_2N] + 3040 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

with (1) and (3), he obtained the following result:

$$2[Fe_4N] + 2NH_3 = 4[Fe_2N] + 3H_2 - 18760 \quad \ldots\ldots \quad (5)$$

The author obtained the equilibrium equations of the reaction (4) and (5) by the use of the Nernst's heat theorem in order to compare them with the observed equilibrium data obtained by E. Lehrer[2] at high temperatures. Lehrer's data are not obtained from pure Fe_2N, Fe_4N, Fe but from solid solutions ε, γ', α. However, γ' and α may be regarded as almost same as pure Fe_4N and Fe respectively, therefore the author found it convenient to compare these data with his equation. ε can not be regarded as equal to pure Fe_2N but the author dared to compare his equation with these experimental data in the following way: Considering that the atomic heat of nitrogen is of course less than 6.4, he calculated the atomic heat of nitrogen from the observed molecular heats of some nitrogen compounds according to Neumann and Kopp's law assuming the atomic heat of oxygen to be 4, that of hydrogen to be 2.3 and those of other elements to be 6.4 each.

Nitrogen compounds.	Calculated atomic heat of nitrogen.
NO_3Na	3.4
$(NO_3)_2Ba$	3.75
$(NO_3)_2Sr$	3.95
NH_4Cl	4.4
NO_3K	5.7
	4.24 (mean).

(1) G. Fowler, Ph. J. Hartog, loc. cit.
(2) E. Lehrer, loc. cit.

The mean atomic heat (4.24) thus obtained was used as the atomic heat of nitrogen in calculating the molecular heats of iron nitrides. From the above mentioned observed result, the heat of formation of Fe_4N (W_1) is expressed in the following equation:

$$4[Fe_4N] = 8[Fe] + N_2 - W_1 \qquad 17°C. \ldots\ldots\ldots\ldots (6)$$

where $W_1 = 8920$. On the assumption that W_1 varies with the temperature, W_1 may be expressed by a series containing only integral powers of T:

$$W_1 = W_{01} + 3.5\,T + \alpha T^2 .$$

Differentiating with respect to T,

$$\frac{dW_1}{dT} = \sum nC_p = 3.5 + 2\alpha T . \qquad \text{where} \quad \sum n = 1 .$$

Assuming the atomic heat of iron to be 6.0, the molecular heat of gaseous nitrogen to be 6.9 and that of Fe_4N to be $6\times4+4.24 = 28.24$, we obtain

$$\alpha = \frac{6.9 + 8\times6 - 2\times28.24 - 3.5}{2\times290} = -0.008759 .$$

Therefore $$W_1 = 8642 + 3.5\,T - 0.008759\,T^2$$

The equiliblium equation of the reaction (6) can readily be obtained as shown below: The chemical constant of nitrogen is 2.6. Accordingly,

$$\sum m = 1 , \qquad \sum mI = 2.6$$

Therefore,

$$\log P_{N_{2(1)}} = -\frac{8642}{4.571\,T} + 1.75\log T - \frac{0.008759T}{4.571} + 2.6 \ldots\ldots (7)$$

According to F. Haber[1], the variation of the equilibrium constant of ammonia is expressed by the following equation:

$$\log K_p = -\frac{4196}{T} + 5.0176\log T + 0.0002012\,T - 0.372\times10^{-6}T^2 - 4.2 \quad (8)$$

From (7) and (8), the equilibrium equation of the reaction (4) can readily be obtained as shown below:

$$\log K_{p_1} = -\frac{2305}{T} + 3.2676\cdot\log T + 0.0021174\,T - 3.72\times10^{-7}T^2 - 6.8 \quad (9)$$

(1) F. Haber, *Z. Elektrochem.*, **20** (1914), 597.

According to G. Fowler, Ph. J. Hartog[1], the heat of formation of Fe_2N is expressed in the following equation:

$$2[Fe] + N = 2[Fe_2N] + 3040 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

From (1) and (2), we obtain

$$4[Fe_2N] = 2[Fe_4N] + N_2 - 3240 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

$$3240 = W_2$$

On the assumption that W_2 varies with the temperature, W_2 may be expressed similarly as in the case of W_1 as follows:

$$W_2 = W_{02} + 3.5\,T + \alpha T^2 .$$

Similarly, $$\frac{dW_2}{dT} = \sum nC_p = 3.5 + 2\alpha T , \qquad \text{where} \quad \sum n = 1 .$$

Assuming the molecular heat of Fe_4N to be 28.24, that of gaseous nitrogen to be 6.9 and that of Fe_2N to be $6 \times 2 + 4.24 = 16.24$, we obtain

$$\alpha = \frac{6.9 + 2 \times 28.24 - 4 \times 16.24 - 3.5}{2 \times 290} = -0.008759 .$$

Therefore $$W_2 = 2962 + 3.5\,T - 0.008759\,T^2$$

The equilibrium equation of the reaction (10) can similarly be obtained. As previously shown,

$$\sum m = 1 , \qquad \sum mI = 2.6 .$$

Therefore,

$$\log P_{N_{2(2)}} = -\frac{2962}{4.571\,T} + 1.75 \log T - \frac{0.008759\,T}{4.571} + 2.6 \quad \ldots\ldots \quad (11)$$

From (11) and (8), the equilibrium equation of the reaction (5) can readily be obtained as before:

$$\log K_{p_2} = -\frac{3548}{T} + 3.2676 \cdot \log T + 0.0021174\,T - 3.72 \times 10^{-7} T^2 - 6.8 \quad (12)$$

The agreement of the equilibrium constants at high temperatures between the calculated values according to the equations (9) and (12) and those observed by E. Lehrer[2] is quite satisfactory as shown in Table 7 and Fig. 5.

(1) G. Fowler, Ph. J. Hartog, loc. cit.
(2) E. Lehrer, loc. cit.

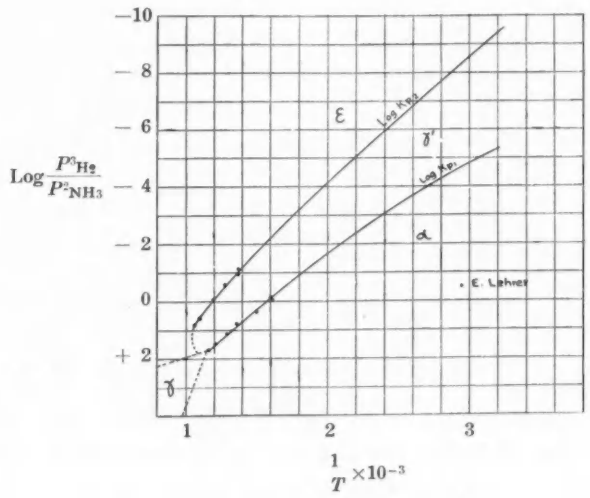

Fig. 5. Variation of equilibrium constants of
$8\,Fe + 2NH_3 = 2Fe_4N + 3H_2$ (Log K_{p1})
$2\,Fe_4N + 2NH_3 = 4\,Fe_2N + 3H_2$ (Log K_{p2})
with temperature.

Table 7. Equilibrium constants of reactions:
$8Fe+2NH_3 = 2Fe_4N+3H_2$
$2Fe_4N+2NH_3 = 4Fe_2N+3H_2$
at various temperatures.

$T°K$	$8Fe+2NH_3 = 2Fe_4N+3H_2$ Log $\frac{P^3_{H_2}}{P^2_{NH_3}}$		$T°K$	$2Fe_4N+2NH_3 = 4Fe_2N+3H_2$ Log $\frac{P^3_{H_2}}{P^2_{NH_3}}$	
	Log K_{p_1} (Author)	Log K_{p_1} (Lehrer)		Log K_{p_2} (Author)	Log K_{p_2} (Lehrer)
618	−0.243	−0.0637	729	−0.966	−1.123
623	−0.195	−0.1154	730	−0.957	−0.968
668	+0.228	+0.346	783	−0.444	−0.589
734	+0.779	+0.752	835	+0.007	−0.060
773	+1.070	+1.107	905	+0.553	+0.600
827	+1.445	+1.473	940	+0.802	+0.845
862	+1.669	+1.675			

The author deduced the following two empirical equations from the measured heat of formation at an ordinary temperature, in order to see whether these equations could express the observed data of E. Lehrer[1] or not:

$$\log K_{p_1}' = -\frac{13080}{4.571\,T} + 4.775$$

$$\log K_{p_2}' = -\frac{18760}{4.571\,T} + 4.775$$

At 734° K and 773° K, the observed equilibrium constants of the reaction (4) are +0.752 and +1.107 respectively while the corresponding calculated values are +0.876 and +1.073 respectively ($\log K_{p_1}'$). And at 730° K and 835° K, the observed data of the reaction (5) are −0.968 and −0.06 respectively while the corresponding calculated values are −0.847 and −0.140 ($\log K_{p_2}'$). In this case the agreement between the observed and calculated values is fairly good.

V. Electrochemical Properties of Iron Nitrides. As described in the previous paper[2], single potential of nitrified iron in ferrous sulphate solution is greatly influenced by the presence of ferric ion. The author measured the single potential of ε, which was confirmed by X-ray to contain no iron.

ε-phase immersed in the ferrous sulphate solution (1 normal) free from ferric ion showed the potential of

$$\varepsilon_h = -0.448 \text{ volt.}$$

which corresponds to the potential of powdered iron, but that immersed in the same solution containing 7 per cent. ferric ion showed the potential of

$$\varepsilon_h = +0.5708 \text{ volt.}$$

It is clear that the presence of ferric ion or oxygen changes the iron nitride into the passive state and that the single potential of iron nitride reported by F. Hanaman[3] is nothing more than that of the passive iron nitride.

If the iron nitride does not show the passive state in the ammonia solution, cells may be constructed by suitable combination of nitrides and hydrogen electrode, and by measuring the electromotive force of these cells, equilibrium constants of the reactions:

(1) E. Lehrer, loc. cit.
(2) S. Satoh, *Am. Inst. Min. Met. Eng., Tech. Publ.*, No. 447 (1932).
(3) F. Hanaman, Dissertation Berlin, (1913).

$$8\,[Fe]+2NH_3 = 2\,[Fe_4N]+3H_2 \quad \ldots\ldots\ldots\ldots\ldots (4)$$

$$2\,[Fe_4N]+2NH_3 = 4\,[Fe_2N]+3H_2 \quad \ldots\ldots\ldots\ldots (5)$$

could be directly measured.

ε-phase immersed in 1-normal ammonia solution shows the potential of

$$\varepsilon_h = +0.199 \text{ volt},$$

as shown in Fig. 6, but that immersed in the same solution free from oxygen shows the potential of

$$\varepsilon_h = -0.713 \text{ volt}.$$

As may be seen, iron nitride shows no sign of changing into the passive state in the oxygen free ammonia solution.

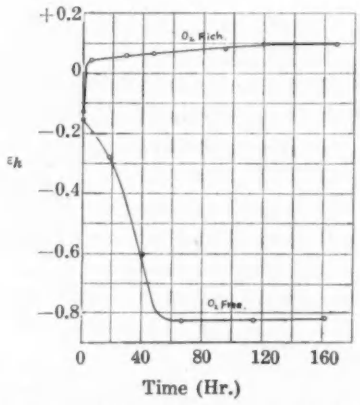

Fig. 6. Potential measurement of iron nitride 1-normal ammonia solution which contained oxygen or not.

If P_{H_2} denoted the partial pressure of hydrogen over ammonia solution and P_{NH_3} that of ammonia, and K_{p_1}, K_{p_2} the equilibrium constants of reactions (4) and (5) respectively, the electromotive force of the cells:

$$Fe\,|\,Fe+Fe_4N\,|\,NH_3\,|\,[PtPt]\,H_2$$

$$Fe_2N+Fe_4N\,|\,Fe_2N\,|\,NH_3\,|\,[PtPt]\,H_2$$

could be expressed in the following equations :

$$E_1 = \frac{RT}{nF}\left(\log K_{p_1} - \log \frac{P_{H_2}^3}{P_{NH_3}^2}\right)$$

$$E_2 = \frac{RT}{nF}\left(\log K_{p_2} - \log \frac{P_{H_2}^3}{P_{NH_3}^2}\right)$$

where $n = 6$ and $T = 308$. The values of $\log K_{p_1}$ and $\log K_{p_2}$ calculated from (9) and (12) are respectively -5.534 and -9.57. The partial pressure of ammonia over 1-normal ammonia solution obtained from the curve based on the measurements of W. Gaus[1], R. Abegg and H. Riesenfeld[2] is 22.1 mm. at 35°C. Therefore, the values of P_{NH_3} can be calculated by the formula of J. Lock and J. Forssall[3] as follows :

$$P_{NH_3} = \frac{22.1 \times n + 0.18\, n^2}{760} = 0.03095 \text{ at.},$$

where $n = 1.055$.

According to E. P. Perman[4], the partial pressure of water over 1.055 normal ammonia solution can be calculated by the following formula :

$$p_0 = P \cdot (1 - x) = 41.43 \text{ mm.},$$

in which p_0 are the partial pressures of water over the solutions, P are the pressures of pure water at the same temperature, and x is the fractional amount of ammonia in 1 gr. of the solution.

Therefore, the values of P_{H_2} can be calculated by the following formula :

$$P_{H_2} = \frac{760 - P - p_0}{760} = \frac{695.1}{760} = 0.9146 \quad \text{at.}$$

Therefore,

$$E_1 = \frac{0.0001983 \times 308}{6}(-5.534 - 2.90) = -0.0859 \text{ volt.}$$

$$E_2 = \frac{0.0001983 \times 308}{6}(-9.57 - 2.90) = -0.1269 \text{ volt.}$$

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(1) W. Gaus, *Z. anorg. Chem.*, **25** (1900), 236.
(2) R. Abegg, H. Riesenfeld, *Z. physik. Chem.*, **40** (1902), 90.
(3) J. Lock and J. Forsall, *Am. Chem. J.*, **31** (1904), 268.
(4) E. P. Perman, *Trans. Chem. Soc.*, **79** (1901), 718; **83** (1903), 1168.

With the object of ascertaining these results, the author made experiments with the apparatus shown in Fig. 7. ε, $\varepsilon + \gamma'$, $\gamma + \alpha$, and α, the compositions of which were determined by chemical analyses and X-ray, were used as specimens. α and $\varepsilon+\gamma'$, compressed in cylindrical form, were soldered at their ends with copper wire. The soldered ends of the specimens α and $\varepsilon+\gamma'$ were inserted into a glass tube a and b respectively, filled with solid paraffin to prevent the solution from entering into the soldered part. In e and f the powders of $\gamma' + \alpha$ and ε were introduced respectively. And g was filled with quartz sand purified with aqua regia. h is a hydrogen electrode and the purified hydrogen was passed through the tube i, and

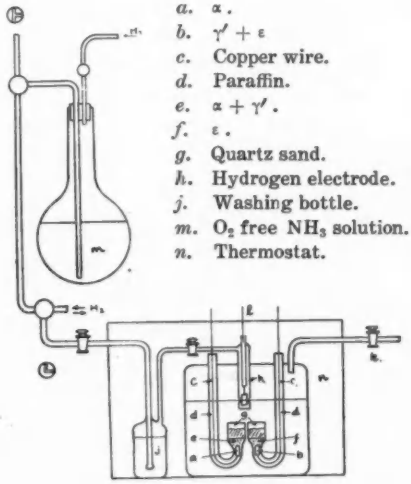

Fig. 7. Apparatus for measurement of the E. M. F. of the iron nitride cell.

through a solution of ammonia of the same concentration as was contained in the cell. l, c being connected with Leeds and Northrup potentiometer, the electromotive force of the cell was measured. The oxygen free ammonia solution was poured into the cell through m. The temperature of the cell was kept constant (35° ± 0.2°C.) by means of the air thermostat. The results obtained are shown in Table 8, and the time voltage curves are shown in Figs. 8 and 9.

As may be seen from the curves, very constant voltage was obtained in each case and the final constant voltages were shown as below :

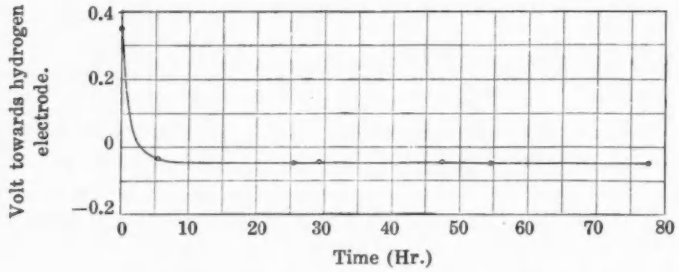

Fig. 8. Time voltage curve of iron nitride cell.
$\alpha \,|\, \alpha+\gamma' - 1.055\,\mathrm{n}\cdot NH_3 - |\,[\,PtPt\,]\,H_2$ at 35°C.

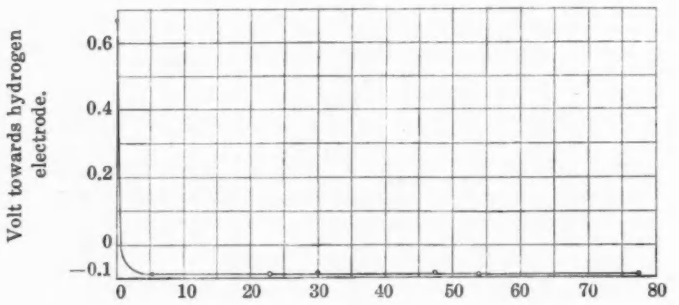

Fig. 9. Time voltage curve of iron nitride cell.
$\gamma' + \varepsilon \,|\, \varepsilon - 1.055\,\mathrm{n}\cdot NH_3 - |\,[PtPt]\,H_2$ at 35°C.

Table 8.

Potential measurement of iron nitride cells.

Temp. (°C.)	Time in NH_3 solution. (Hr.)	$\alpha\|\alpha+\gamma' - 1.055\,\mathrm{n}\cdot NH_3 - \|[PtPt]H_2$ volt.	$\gamma'+\varepsilon\|\varepsilon - 1.055\mathrm{n}\cdot NH_3 - \|[PtPt]\,H_2$ volt.
35	0	−0.3501	−0.6693
,,	5.5	0.03232	0.08595
,,	23	0.04965	0.08447
,,	30	0.04564	0.08145
,,	47.5	0.04507	0.07974
,,	54.	0.04911	0.08309
,,	77.5	0.04800	0.08270

$$\underset{(-)}{\alpha} \mid \alpha+\gamma' - -1.055\ \text{n-NH}_3 - - \mid [\text{PtPt}] \underset{(+)}{\text{H}_2}, \quad E_1' = -0.048 \text{ volt},$$

$$\underset{(-)}{\gamma'+\varepsilon} \mid \varepsilon - -1.055\ \text{n-NH}_3 - - \mid [\text{PtPt}] \underset{(+)}{\text{H}_2}, \quad E_2' = -0.0827 \text{ volt}.$$

These values do not agree with the calculated ones. Differences between the observed and calculated values are about 0.04 volt at 35°C. and about 0.07 volt at 0°C. Although E_1-E_2 and $E_1'-E_2'$ seem to agree fairly well, this cell could not be regarded as a reversible iron nitride cell. The author tested various solutions such as ammonical methyl alcohol, ammoniacal ethyl alcohol, Diver's solution and liquid ammonia containing potassium amide, but was not able to obtain the reversible iron nitride cell.

Summary.

1. The heat of formation of Fe_4N was determined by means of calorimeter.

2. The molecular heats of Fe_2N and Fe_4N were calculated by applying the Neumann and Kopp's law and obtained the equilibrium equations of the systems: Fe, Fe_4N, NH_3, H_2 and Fe_4N, Fe_2N, NH_3, H_2 from the observed heat of formation of Fe_4N by using the Nernst's heat theorem. The calculated values by these equations agree well with the equilibrium data obtained at high temperatures.

3. Various iron nitrides were prepared and their compositions were accurately determined by X-ray.

4. The electrochemical properties of the iron nitrides were studied and the passive state of iron nitride was made clear.

5. The reversible property of the iron nitride cell was examined.

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STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. IV. INFLUENCE OF SUBSTITUENTS ON A PINACONE IN ITS REACTIVITY. REDUCTION OF DI-*p*-METHOXY-BENZOPHENONE.

By Masao MIGITA.

Received September 17th, 1932. Published October 28th, 1932.

When trisubstituted α-glycols are treated with dehydrating agent, the influence of substituents can be seen chiefly in the mode of molecular rearrangement, and the reaction products are ketones or aldehydes.(1) αα-Dimethyl-β-acetyl glycol, $(CH_3)_2C(OH).CH(OH).COCH_3$, is the only instance known in which a trisubstituted α-glycol undergoes simultaneously molecular rearrangement and dissociation into ketone and carbinol by the action of rearranging agents.(2) The author has attributed the dissociation of this glycol to the presence of unstable linkage in the molecule between α and β carbon atoms. If it be so, aromatic pinacones are quite possible to give simultaneous reaction of rearrangement and dissociation under the same conditions, because they bear close resemblance to hexa-aryl ethanes with respect to the negativities of substituents and are assumed to have unstable linkages between the two adjacent carbon atoms in chain, owing to their strongly positive polarities. In fact, all known aromatic pinacones split into corresponding ketones and carbinols at their melting points, and particularly in the case of tetra-*p*-bromobenzopinacone, it is reported that pinacoline rearrangement and dissociation into ketone and carbinol take place simultaneously by the action of acetyl chloride.(3) Under the same conditions, not a single case of dissociation has been reported with other aromatic pinacones with highly negative groups such as diphenyl, fluoryl or xanthyl.(4)

For the purpose of drawing some conclusion on the influence of negative substituents upon the reactivities of pinacones by collecting a series of new data, tetra-*p*-methoxybenzopinacone is first studied, because it contains anisyl radical which is regarded the most negative organic radical, and yet all that we can find in literature about it, is

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(1) $RR'C(OH).CHR''(OH) \rightarrow \begin{cases} RR'R''C.CHO & \text{(Semihydrobenzoin rearrangement).} \\ RR'CH.CO.R'' & \text{(Vinyl dehydration).} \\ RCO.CHR'R'' & \text{(Semipinacoline rearrangement).} \end{cases}$

(2) Migita, this Bulletin, **4** (1929), 225–234.

(3) Montagne, *Rec. trav. chim.*, **43** (1924), 126–142.

(4) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 236–257.

the following few lines with a proviso "unpublished" that anisyl pinacone, $(CH_3OC_6H_4)_2C(OH).C(C_6H_4OCH_3)_2(OH)$, melts at 182°C. and remelts at 117–118°C., if the melting point is remeasured after one hour with the same sample.[1]

Reduction of Di-*p*-Methoxybenzophenone. In order to prepare the pinacone in question, the reduction of di-*p*-methoxy-benzophenone was tried by the following methods, which are usually employed for this purpose, namely, reductions by zinc dust and acetic acid, by absolute alcohol under direct sunlight, and by binary mixture of magnesium and its iodide in ether-benzene solution.

According to the authors[2] the third method seems most suitable for preparation of pinacones with highly negative substituents, for it gives not only very satisfactory yields (75–100%) on many aromatic ketones, but also it enables us to reduce ketones such as dibiphenylyl ketone, fluorenone, and xanthone, of which reduction to corresponding pinacones has been proved unsuccessful by other methods. However, in the case of dimethoxy-benzophenone, the reaction did not proceed smoothly and resulted in formation of a tarry matter, though the reaction was carried out under various conditions.

As the above method had proved unsuccessful, reduction by hot glacial acetic acid and zinc dust was tried. The reaction product, however, was not the expected pinacone, but the corresponding pinacoline, the rearrangement product of the pinacone. A similar case has been reported in reduction of *p*-methoxy-benzophenone.[3] Supposing that this pinacoline formation was due to heating the reaction mixture, the reduction was repeated at room temperature by using the same reducing agents. But the product was not again the pinacone but the pinacoline. That this pinacoline is of β-form, and not of α-form with oxide-ring, was proved by its stability toward acetyl chloride, for the latter should be easily converted to the former by this treatment.

$$(CH_3OC_6H_4)_2C\!-\!\underset{\alpha\text{-form.}}{\overset{\diagdown O \diagup}{}}\!-\!C(C_6H_4OCH_3)_2 \xrightarrow{CH_3COCl} \underset{\beta\text{-form.}}{(CH_3OC_6H_4)_3C.CO.C_6H_4OCH_3}$$

Lastly tetramethoxy-benzopinacone was obtained by reducing the ketone under direct sunlight with absolute alcohol in a sealed tube. This pinacone decomposes on melting, usually into dianisyl ketone and

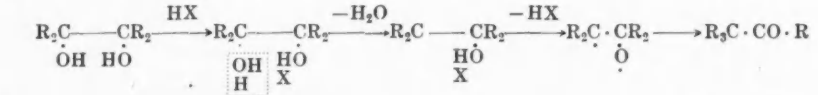
(1) Bouvet, *Bull. soc. chim.*, [4], **15** (1915), 209.
(2) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 236–257.
(3) Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37** (1925), 430.

dianisyl carbinol. Facility of rearrangement is one of the characteristics of this pinacone, and slightly warmed acetic acid is sufficient to convert it to the pinacoline. Though a close experiment was carried out in order to know if this pinacone undergoes dissociation as well as rearrangement by the action of acetyl chloride, no dissociation products were detected.

On the Facility of Rearrangement of Pinacones. (a) *Effect of Highly Negative Substituents.* The effect of negative substituents upon the reactivities of pinacones can be seen clearly in the reduction of benzophenone and its methoxy-derivatives by zinc dust and acetic acid (See the following table).

Reducing agent / Ketone	Zinc dust and acetic acid	
	At room temperature	At higher temperature
$CH_3OC_6H_4.CO.C_6H_4OCH_3$	Pinacoline	Pinacoline
$CH_3OC_6H_4.CO.C_6H_5$	Pinacone[2]	Pinacoline[1]
$C_6H_5.CO.C_6H_5$		Pinacone[3]

In dimethoxy-benzophenone, pinacoline formation from ketone takes place even at room temperature, and in the case of methoxy-benzophenone at high temperature, while in benzophenone, pinacoline formation is not observed under these conditions. In order to convert benzopinacone into the pinacoline by the action of acetic acid, it is necessary to heat it in a sealed tube, at 180–200°C. Thus we can see a marked increase of reactivity of the pinacone caused by successive introductions of methoxy-radical into the benzophenone molecule; which will be easily explained from the mechanism of pinacoline rearrangement discussed in foregoing papers. According to the author's interpretation,[4] the first stage of the pinacoline rearrangement is the attraction between one of the hydroxyl groups of the pinacone and the hydrogen ion of the acid, and the reaction proceeds in the following manner.



(1) Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37** (1925), 430.
(2) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.
(3) Zagumenni, *Ber.*, **14** (1881), 1402.
(4) Migita, this Bulletin, **3** (1928), 312.

Evidently, the attraction between hydrogen ion and the hydroxyl group is stronger, according as the negativity of the latter is larger; then it follows naturally from the theory of induced alternate polarity that pinacones with highly negative substituents should undergo rearrangement with great facility. And in the case of tetramethoxy-benzopinacone, owing to the extreme negativity of anisyl radical, its hydroxyl groups may be supposed to have so strongly negative polarity as the rearrangement takes place even by the action of a weak organic acid at ordinary temperature.

(b) *Function of a Small Quantity of Iodine in Pinacoline Rearrangement.* Gomberg and Bachmann[1] reported that a crystal or two of iodine in hot acetic acid is sufficient to convert a number of aromatic pinacones, including benzopinacone, to the pinacolines. The function of iodine in this case is supposed either to increase the negativity of oxygen atom of hydroxyl groups by attracting its hydrogen atom, or to produce hydroiodic acid by reacting with acetic acid, which behaves as rearranging agent. Then, in the case of pinacones with extremely negative groups the rearrangement can occur by the action of acetic acid even in the absence of iodine, as seen in the case of tetramethoxy- and dimethoxy-benzopinacones. Besides these, sym. di-*p*-methoxy-di-*p*-ethoxy-benzopinacone, sym. di-*p*-methoxy-di-*p*-phenyl-benzopinacone and sym. di-*p*-anisyl-di-β-naphthyl glycol may be cited in illustration, which will be described in other papers.

Experimental Part.

p-Anisic Acid. M. p. 182°C. Behrens[2] describes that it crystallises in needles of straight extinction and of negative character, but the crystals must be chiefly of oblique extinction, since they belong to monoclinic system and the face most developed is (110).[3] This was confirmed by actual observation.

Di-p-Methoxy-Benzophenone. This ketone was prepared from *p*-anisole and anisoyl chloride.[4] It crystallises from alcohol in plates or needles with oblique extinction, melts at 143°C., and is difficultly soluble in ligroin and ether, and readily in acetone and chloroform. In concentrated sulphuric acid it dissolves with yellow colouration, which was reported to be red in literature.[4]

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(1) Loc. cit.
(2) Behrens-Kley, "Organische Mikrochemische Analyse," p. 79.
(3) Groth, "Chemische Krystallographie" IV, p. 504.
(4) Schnackenberg and Scholl, *Ber.*, **36** (1903), 654.

Reduction of Di-p-Methoxybenzophenone.

Reduction by Zinc-Dust and Acetic Acid. (a) *At High Temperature.* To a boiling solution of 2.4 gr. of the ketone in 15 c.c. of acetic acid, 6.5 gr. of zinc dust were added in portions. The solution, assuming light greenish tint, was kept gently boiling for 3 hours. Excess of zinc dust was filtered hot from solution and washed thrice with hot glacial acetic acid. The filtrate and washings were poured into water. Slightly greenish precipitates were gathered and purified from alcohol. It forms slender needles with straight extinction and of negative character, melting at 140–141°C. with slight decomposition and solidified in a glassy mass. It is readily soluble in acetone and chloroform, sparingly in ether and hot ligroin, and moderately in alcohol. It dissolves in concentrated sulphuric acid with intense mixed colours of green, blue and violet which changed to purple on standing.

Analysis. Subst. = 0.1613; CO_2 = 0.4549; H_2O = 0.0884 gr.
Found: C = 76.9; H = 6.14%.
Calc. for $C_{30}H_{28}O_5$ (tetramethoxybenzopinacoline): C = 76.9; H = 5.98%.

Action of Acetyl Chloride. In order to determine whether this pinacoline is of α- or β-form, it was treated with acetyl chloride in benzene solution as in the manner described later. The purified product was proved to be unchanged pinacoline. Thereby it is shown that the pinacoline is of β-form.

Hydrolysis. After boiling 0.5 gr. of this pinacoline with alcoholic potash for 12 hours, the product was poured into water, and the filtered solution was acidified with hydrochloric acid. Separated acid was recrystallized from hot water and was easily identified as *p*-anisic acid.

(b) *At Room Temperature.* Two grams of the ketone were dissolved in sufficient glacial acetic acid to keep it in solution at room temperature and an excess of zinc dust was added to the solution. After allowing the mixture to stand at room temperature (20–30°C.) for four days, the solution, filtered from unchanged zinc dust, and poured into a large quantity of water. Yellowish precipitates were washed with cold ether and then recrystallised from alcohol. The product crystallises in colourless fine needles which melt at 141°C. and dissolve in concentrated sulphuric acid with mixed colours of intense green, blue and purple. It was identified as tetra-*p*-methoxy-benzopinacoline by mixed melting point test.

Reduction by Absolute Alcohol under Direct Sunlight. Four grams of dianisyl ketone and 20 c.c. of absolute alcohol were sealed in a tube and exposed in sunlight. In the first two days, the change of

the crystalline appearance in the tube was observed and the solution assumed yellowish tint. After a week, the tube was opened and granular crystals were filtered off from the solution smelling richly of acetaldehyde. The crystals were treated with hot 95% alcohol repeatedly to remove unchanged dianisyl ketone, until the residue, obtained by evaporation of the alcoholic solution, gives with concentrated sulphuric acid intense blue coloration, free from yellow tint produced when the ketone is present. This procedure accompanies considerable loss of pinacone, but we can obtain the pinacone with reliable melting point only in this way. The product crystallises from a quantity of alcohol in white microscopic prisms with straight extinction and of positive character. It decomposes at melting point which is 176°C. when the temperature of the bath is slowly raised, and 181°C. when heated quickly. It remelts, after solidification, at 123–125°C., while 117–118°C. is given by Bouvet.(1) It dissolves in concentrated sulphuric acid imparting to the solution mixed colours of intense blue and violet.

Anal.: Subst. = 0.1118; CO_2 = 0.3028; H_2O = 0.0636 gr.
Found: C = 73.8; H = 6.34%.
Calc. for $C_{30}H_{30}O_6$ (tetramethoxybenzopinacone): C = 73.9; H = 6.18%.

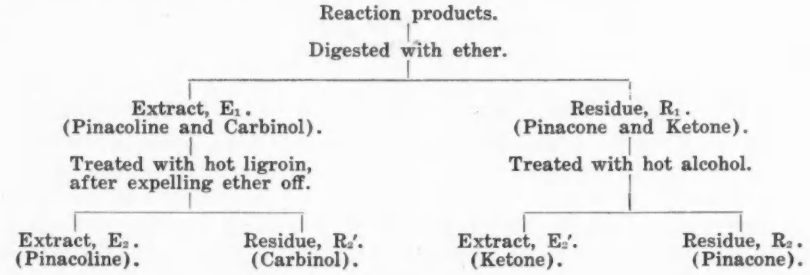
Reduction by Gomberg's Binary Mixture. To a boiling suspension of 1 gr. of magnesium in the solvent consisting of 15 c.c. of absolute ether and 20 c.c. of benzene, 1 gr. of iodine was added and the content was kept briskly boiling until practically colourless solution was obtained (about for one hour). The solution of magnesium iodide was cooled, to which 1 gr. of di-*p*-methoxy-benzophenone dissolved in 10 c.c. of warm benzene was added, and the content was shaken. During this process, heat was evolved and the solution became opaque and assumed brownish-red colour. The solution was gradually clarified and coloured deep red, while magnesium was coated with sticky substance, presumably owing to the formation of complex between the ketone and magnesium iodide. The content was shaken with repeated additions of fresh magnesium but every time it was coated immediately. When the reaction mixture was shaken for ten hours with a great excess of magnesium (a hundred times of theoretical amount), or heated to boiling to complete the reaction with efficient condenser of which upper end was stoppered, the solution was coloured dark and magnesium was uncoated. On hydrolysis, brown rosinous matter was obtained which gave yellowish-brown amorphous substance (about 0.1 gr.) when purified from alcohol. The product, however, was not the pinacone nor the pinacoline in question, since it dissolves in concentrated sulphuric acid with reddish-brown colouration.

Some Reactions of Tetramethoxybenzopinacone.

Analytical Procedure. Separation of the pinacone, and its rearrangement and decomposition products in the presence of one another,

(1) Loc. cit.

which is indispensable in the study of reactions of tetramethoxybenzopinacone, was effected by the following scheme:



Of course, complete separation is attained by no means in this way, but it is not difficult to obtain a pure compound by further recrystallisation. For their identification, besides melting point and mixed melting point test, the colour reaction with concentrated sulphuric acid proved of good service.

Decomposition at Melting Point. 0.2 Gr. of the pinacone was heated at 185°C. for one hour, the cooled mass was powdered and analysed after the above process. The same white crystalline substance was obtained both from R_1 and E_2 which was identified as dimethoxybenzophenone. Repeated recrystallization of R_2', a semi-solid, from chloroform and ligroin, did not succeed in isolation of a compound with definite melting point. But it can be assumed to be dimethoxybenzohydrol by its behaviour toward solvents and by red colouration produced when dissolved in concentrated sulphuric acid.

Rearrangement of the Pinacone. (a) *Action of Hot Glacial Acetic Acid.* 0.1 Gr. of the sample was heated with 2 c.c. of glacial acetic acid at 100°C. for ten minutes, the content was poured into water and analysed. Tetramethoxybenzopinacoline, which melts at 140°C. with slight decomposition and solidifies in a glassy mass was obtained.

(b) *Action of Acetyl Chloride.* Two grams of the pinacone was dissolved in a mixture of 50 c.c. of dry benzene, 20 c.c. of acetyl chloride and 10 c.c. of glacial acetic acid, and was gently boiled for eight hours. After distilling the benzene off, the content was treated in the same way as in the last case. Tetramethoxybenzopinacoline was the only product isolated, dianisyl ketone and dianisyl carbinol being not detected.

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STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. V. RELATIVE ELECTRONEGATIVITIES OF *p*-METHOXY-PHENYL AND *p*-ETHOXY-PHENYL RADICALS.

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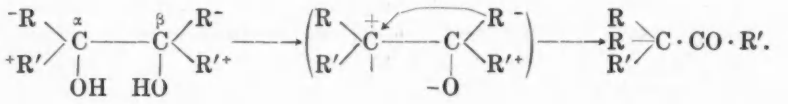
The author has observed that tetra-*p*-methoxybenzopinacone shows extreme facility to undergo molecular rearrangement and has attributed this behaviour to accumulation of strongly negative substituents in the molecule.[1] In order to confirm this assumption by another example on the one hand, and to compare relative electronegativities of *p*-methoxyphenyl and *p*-ethoxyphenyl radicals on the other hand, the reduction of 4-methoxy-4′-ethoxy-benzophenone and the rearrangement of the corresponding pinacone are studied. The principle of the determination of relative electronegativities of organic radicals by pinacoline rearrangement is based on the fact that in the rearrangement of *symmetrical* pinacone, $RR'C(OH)\cdot C(OH)RR'$, migration of the more negative radical, say R, takes place principally, and pinacoline $RRR'\ C\cdot CO\cdot R'$ is the chief product.[2] This selective migration of the substituents in the rearrangement of a symmetrical pinacone can be interpreted as follows:



The α carbon atom in the fraction of molecule, $RR'\dot{C}\cdot CO\cdot RR'$, which is assumed to be produced intermediately, is highly negatively polarized, since this carbon atom has been deprived of a part of its bond-forming electrons with the elimination of hydroxyl group. Therefore, if a radical migrates to this carbon atom from the other, the more negative radical is naturally assumed to wander with greater easiness.

As for the relative electronegativities of lower alkyl radicals, the results given by different methods are not concordant, but it is generally accepted that no parallelism exists between electronegativities of alkyl

(1) Migita, this Bulletin, **7** (1932), 336.

(2) We can find a series of such cases in literature, for example, $R = C_6H_5$, $R' = CH_3$; $R = CH_3OC_6H_4$, $R' = C_6H_5$; $R = C_6H_5C_6H_4$, $R' = C_6H_5$.

radicals and the number of their carbon atoms and that methyl radical is more electronegative than ethyl.[1]

Now, if methyl radical is more negative than ethyl, in the case of alkoxy-radicals the relation of negativities will be inversed by the theory of induced polarity, ethoxy being more negative than methoxy radical. Nextly when this methoxy or ethoxy radical enters in phenyl radical at para position, the relation of electronegativities between these alkoxyphenyl radicals are the same with that between the original alkoxy radicals, since the effect of the negativities of alkoxy radicals appear alternately in the carbon atoms of the benzene ring. Thus *p*-ethoxyphenyl will be more negative than *p*-methoxy radical.

Now, in the actual rearrangement of sym. dimethoxy-diethoxybenzopinacone, migration of ethoxy radical took place almost exclusively and 4-methoxyphenyl-bis(4′-ethoxyphenyl)-4″-methoxybenzoyl-methane, $(C_2H_5OC_6H_4)_2(CH_3OC_6H_4)C.CO.C_6H_4OCH_3$ was produced. This shows, as expected, that *p*-ethoxyphenyl radical is more negative than *p*-methoxyphenyl, and thereby, it gives an indirect proof on the more negative character of methyl radical than ethyl.

On reduction by glacial acetic acid and zinc dust, 4-methoxy-4′-ethoxybenzophenone gives corresponding pinacoline, as in the case of dimethoxybenzophenone. This is to be expected, as both the ketones are accumulated with highly negative radicals.

It is highly interesting that a fair quantity of the pinacoline, but no pinacone, was isolated from reduction products of this ketone by absolute alcohol under direct sunlight, while in the case of dimethoxybenzophenone, pinacone was the only product. It is inferable, thereby, that between these two substituted benzophenones the former exceeds the latter in its reactivity, which is consistent with the fact that *p*-ethoxyphenyl is more negative than *p*-methoxyphenyl radical, since the reactivity of a pinacone is considered to increase according as the negativities of substituents are raised.[2] As for the mechanism of pinacoline formation by this reduction, it was assumed if a minute quantity of

(1) $C_3H_7>CH_3>C_2H_5$, by carbinol method (Skraup, *Ber.*, **55** (1922), 1074).
$CH_3>C_3H_7>C_2H_5$, by pinacoline method (Meerwein, *Ann.* **419** (1919), 121.
$CH_3>C_2H_5>C_3H_7$, by dialkylmercury method (Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130).
Skraup and Meerwein did not use the term "electronegativity," but employed the term "affinity requirement." These two expressions, however, are the same in essence, since "affinity requirement" can be understood from electronic conception of valency as affinity for binding electrons.

(2) Migita, this Bulletin, **7** (1932), 336.

acetic acid was produced by oxidation of alcohol, and if this alcoholic acetic acid behaved as rearranging agent. This assumption, however, was given up for the actual reduction products did not give acidic reaction.

Experimental Part.

4-Methoxy-4′-Ethoxy-Benzophenone, $CH_3OC_6H_4.CO.C_6H_4OC_2H_5$. *p*-Anisoyl chloride, prepared from 15 gr. of *p*-anisic acid and a slight excess of thionyl chloride, was reacted in the presence of 12 gr. of aluminium chloride with 13 gr. of phenetol in carbon bisulphide solution. The reaction proceeded very smoothly and completed in few hours. On hydrolysing the aluminium complex, dark brownish heavy oil was obtained, which solidified in buttery mass by repeated steam distillation alternately in very weak acid and alkaline reactions. From hot alcoholic extract of this buttery mass 4-methoxy-4′-ethoxy-benzophenone crystallised out in scales with pearly lustre, which were drained on porous plate. Recrystallised methoxy-ethoxy-benzophenone melts at 106–107°C., is readily soluble in hot ligroin and cold ether, and difficultly in cold alcohol and acetic acid. When recrystallised from ligroin, the ketone precipitates in gelatinous mass. It dissolves in concentrated sulphuric acid with yellow colour.

Anal.: Subst. = 0.0742; CO_2 = 0.2030; H_2O = 0.0415 gr.
Found: C = 74.7; H = 6.22%. Calc. for $C_{16}H_{16}O_3$ (Ketone): C = 75.0; H = 6.26%.

4-Methoxyphenyl-bis (4′-Ethoxyphenyl)-4″-Methoxybenzoyl-Methane, $(CH_3OC_6H_4)(C_2H_5OC_6H_4)_2C.CO.C_6H_4OCH_3$. (a) *Reduction by Hot Acetic Acid and Zinc Dust.* Three grams of zinc dust were added in portions to gently boiling solution of 1.35 gr. methoxyethoxybenzophenone in 6 c.c. acetic acid. After four hours' boiling, acetic acid solution, filtered from unchanged zinc dust, was poured into a large quantity of water, pale yellowish flocculent precipitates being obtained. The unchanged zinc dust was treated twice with hot acetic acid and the combined extracts were treated in the same way. The crude product was readily soluble in ether, but in the solution it became free from yellow impurities and the ketone separated out as colourless granular crystals. Purifications from other solvents could not bring desired results. It melts at 160°C. and solidifies vitreously. It is readily soluble in benzene, and moderately in hot ligroin but sparingly in cold. It dissolves in concentrated sulphuric acid with dark brown colour which changes to

intense bluish purple. The product was found, by analysis, to be the corresponding pinacoline, but not the pinacone.

Anal.: Subst. = 0.0696; CO_2 = 0.1970; H_2O = 0.0415 gr.
Found: C = 77.2; H = 6.61%.
Calc. for $C_{32}H_{32}O_5$ (Pinacoline): C = 77.5; H = 6.45%.

Constitution. By reduction of methoxyethoxybenzophenone, we may have two isomeric pinacolines, I and II, which will give on hydrolysis with alcoholic potash *p*-anisic acid and *p*-ethoxy-benzoic acid respectively.

(I) $(CH_3OC_6H_4)(C_2H_5OC_6H_4)(C_2H_5OC_6H_4)C-CO-C_6H_4OCH_3$

(II) $(CH_3OC_6H_4)(CH_3OC_6H_4)(C_2H_5OC_6H_4)C-CO-C_6H_4OC_2H_5$

In order to determine which of these two possible pinacolines has been actually obtained, the reduction product was hydrolysed by boiling with 20% alcoholic potash for twelve hours. After distilling off alcohol under diminished pressure, water was added to dissolve the potassium salt of organic acid. The neutral product which present as precipitates was extracted with benzene. The aqueous solution was acidified with sulphuric acid and was extracted with benzene. After removal of the solvent, the acid was treated with boiling water, in which *p*-anisic acid should be readily soluble while *p*-ethoxybenzoic acid only in trace. Actually the product was found dissolved in hot water completely. By repeated recrystallisations from hot water, fine colourless needles melting at 184°C. were obtained, which were identified as *p*-anisic acid by mixed melting point test, and by optical properties of the crystals. Thus the pinacoline was proved to be 4-methoxyphenyl-bis(4′-ethoxyphenyl)-4″-methoxybenzoyl-methane, corresponding to formula I.

(b) *Reduction by Absolute Alcohol under Direct Sunlight.* Methoxyethoxybenzophenone, dissolved in hot absolute alcohol, was sealed in a tube and exposed under direct sunlight. White crystals which fulfilled the tube disappeared in the course of several days and lightly yellowish-brown solution was obtained. The formation of acetaldehyde was easily detected by its peculiar smell and the sharp colour reaction toward Schiff's reagent. On distilling alcohol off under reduced pressure, greenish-gray soft mass was obtained, which was easily soluble in ordinary solvents except petroleum ether and ligroin. The crude product

was dissolved in small amount of alcohol and the solution was kept below 0°C. In the course of few days crystals appeared, from which the mother liquor was decanted off. But as the crystals were still contaminated with sticky impurities, dissolution and cooling were repeated twice, and finally they were purified from ether. The product crystallises in granules, melting at 160°C., and dissolves in concentrated sulphuric acid with colouration of dark brown which changes to intense bluish-purple. No depression of melting point was observed when mixed with the pinacoline obtained by reducing the original ketone by zinc dust and glacial acetic acid. From the fraction readily soluble in alcohol no definite compound could be isolated.

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